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THE ESTERS OF CACODYLPHOSPHONIC ACID. REPORT NO 2

Gil'm Kamay and
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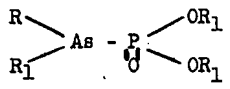
Submitted 18 Nov 1948

In the preceding report (1) by these members of the Chemical Institute imeni Academician A. Ye. Arbuzov, Kazan Affiliate of the Academy of Sciences, USSR, the synthesis of representatives of a new group of arsenophosphoro-organic compounds with the direct single bond, As - P, was described for the first time in chemical literature.

Two comparatively simple methods were employed in the preparation of compounds of this group: the interaction of various secondary halogen arsines either: (1) with alkyl esters of phosphorous acid, or (2) with metal derivatives of diethylphosphorous acid in absolute ether.

The purpose of this report is to summarize results of the investigation of new representatives of esters of cacodylphosphonic acid with the following general formula:



Through the interaction of a sodium salt of dialkylphosphorous acid (where the alkyl radical is C_3H_7 or C_4H_9) with various secondary iodoarsines, a number of esters of cacodylphosphonic acid were synthesized. These esters are shown in the following table along with their physical properties:

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Ester	Structure	Bp at 2 mm in °C	d_o^o	n_D
1. $(CH_3)_2As-P(=O)(OC_3H_7)_2$	Iso	99-99.5	1.1932	1.4761
2. $(CH_3)_2As-P(=O)(OC_4H_9)_2$	Normal	127-128	1.0884	--
3. $(C_2H_5)(n\ C_4H_9)As-P(=O)(OC_4H_9)_2$	Normal	146-147	1.1226	1.4775
4. $(C_2H_5)(iso\text{-}C_4H_9)As-P(=O)(OC_4H_9)_2$	Normal	138.5-139	1.1268	1.4733
5. $(C_2H_5)(C_6H_5)As-P(=O)(OC_3H_7)_2$	Normal	165-166	1.2620	1.5375
6. $(C_2H_5)(C_6H_5)As-P(=O)(OC_4H_9)_2$	Normal	176-176.5	1.2031	1.5304

The esters listed above are colorless liquids with the characteristic unpleasant odor of cacodyls, and can be distilled without decomposition in a stream of inert gas in a high vacuum.

The propyl and also the butyl esters of cacodylphosphonic acid can be saponified by heating with concentrated hydrochloric acid; in the process of saponification, the corresponding alkyl chlorides, the oxides of secondary arsines, and phosphorous acid are liberated.

It was shown also that the alkyl esters of cacodylphosphonic acid are oxidized upon contact with the air, apparently, according to the reaction:

$$2\ R_2As-P(=O)(OR_1)_2 + O_2 \rightarrow R_2As-O-AsR_2 + [(RO)_2PO]_2O.$$

The initial members of the preceding table are oxidized quickly upon contact with the air. The oxidation of the first and second ester, for example, proceeds by the way of a pronounced exothermic reaction.

Preparation of Ethylisobutyliodoarsine

100.5 grams of ethyldiiodoarsine were added to a mixture of 115 milliliters of 10 N solution of NaOH and 150 milliliters of 95-percent alcohol, and into the resulting clear solution were then gradually added 51 grams of isobutyl bromide. After 6 hours, the alcohol was distilled off by boiling on a water bath. Further procedures of this preparation were given previously (2) for an analagous compound.

SECRET

The boiling point of this compound is 103-104 degrees at 13 millimeters, and the yield was 69.8 percent of the theoretical.

0.1257 g of the substance weighed in; 0.10243.911 g AgI

/Note: The figure for the amount of AgI obtained is obviously incorrect./

Found % of I: 43.91

Computed % of I: 44.07

This compound ($C_6H_{14}AsI$) is a clear colorless liquid with an unplesant odor.

Preparation of n-butylester of Methylethylcacodylphosphonic Acid

Into a 500-milliliters round-bottomed flask equipped with a dropping funnel, an agitator, and a reflux condenser, and containing 200 milliliters of absolute ether were introduced 3.2 grams of sodium metal wire. Then through the dropping funnel were added 28.6 grams of dibutylphosphorous acid. Formation of the sodium salt of dibutylphosphorous acid occurred in an exothermic reaction. After adding the total quantity of the acid, the contents of the flask were boiled on a water bath for 2 hours, and the mixture was then cooled prior to the addition of 33 grams of methylethyliodoarsine. Finally, the flask was heated on the water bath for 2 hours, and after cooling, the precipitate of sodium iodide was filtered off and the ether distilled from the filtrate. The substance remaining was distilled in a vacuum in a stream of inert gas. The boiling point was 127-128 degrees; the yield 56 percent of the theoretical.

I. 0.1409 g of the substance weighed in; 0.0695 g As_2S_5

II. 0.1189 g of the substance weighed in; 0.0598 g As_2S_5

Ia. 0.1369 g of the substance weighed in; 26.65 ml NaOH

IIa. 0.1409 g of the substance weighed in; 30.60 ml NaOH 1 ml NaOH; 0.475 mg P

Found % of As: I-23.83; II-24.30; found % of P: I-9.82;II-10.15

Computed % of As: 24.01; computed % of P: 9.94

d_0^{20} 1.0710

$C_{11}H_{26}AsPO_3$

Upon standing in the air for some time this liquid turns dark, oxidizing to form methylethylarsinic oxide.

Oxidation of n-butyl Ester of Methylethylcacodylphosphonic Acid

Twelve grams of this substance were placed in a distillation flask of the A. Ye. Arbuzov type, and air was bubbled through it for 5 hours. The reaction commenced with the liberation of a small quantity of heat. The next day, the contents of the flask were subjected to distillation in a vacuum, and 4.2 grams of substance boiling at 73-74 degrees at 11 millimeters were obtained. A viscous liquid remaining in the flask was not distilled further. Investigation established this as bis-(methylethylarsyl)-oxide, previously prepared by one of these authors /probably Kamay/ as well as by Wigren (3).

SECRET

SECRET

Preparation of Isopropylester of Methylethylcacodylphosphonic Acid

This substance was synthesized by introducing 2 grams of metallic sodium into 17 grams of diisopropylphosphoric acid and 22.5 grams of methylethyliodoarsine. By distillation in a current of CO_2 the following fractions were obtained:

I. 93-98° at 2 mm - 2.6 g

II. 99-100° at 2 mm - 3.19 g

Residue in the flask - 6.5 g

The second fraction in a subsequent distillation yielded a fraction with a boiling point of 99-99.5 degrees at 2 millimeters and 110-112 degrees at 4-5 millimeters.

0.1173 g of the substance weighed in; 0.0645 g As_2S_5

0.1286 g of the substance weighed in; 29.75 ml NaOH

Found % of As: 26.98; found % of P: 10.81

Computed % of As: 26.38; computed % of P: 10.92

$C_9H_{22}AsPO_3$

d_0^{18} 1.1733; n_0^{18} 1.4761

Preparation of n-butylester of Ethyl-n-butylcacodylphosphonic Acid

This compound was synthesized by introducing 3.5 grams of metallic sodium into 31 grams of n-dibutylphosphorous acid and 35 grams of ethyl-n-butyliodoarsine in absolute ether. The exothermic reaction resulted in the formation of a white crystalline residue -- a 52-percent yield of the theoretical.

0.1311 g of the substance weighed in; 0.569 g As_2S_5

0.1399 g of the substance weighed in; 21.7 ml NaOH

1 ml NaOH; 0.5448 mg P

Found % of As: 20.97; found % of P: 8.45

Computed % of As: 21.16; computed % of P: 8.76

$C_{14}H_{32}AsPO_3$ is a colorless, rather viscous liquid (d_0^{20} 1.1048 and n_D^{20} 1.4775) which is quickly oxidized upon contact with the air. The oxidation products were not investigated.

Preparation of n-butyl ester of Ethylisobutylcacodylphosphonic Acid

For this synthesis, 2.08 grams of metallic sodium, 17.6 grams of dibutylphosphorous acid, and 28 grams of ethylisobutyliodoarsine were used and the resulting ethereal extract, distinguished by a weak yellow color, was distilled in a vacuum in a stream of CO_2. Boiling point of the main fraction was 138.5-140 degrees at 2 millimeters, /Note: This value is not the one given in the table, however./ The yield was 17.3 grams or about 54 percent of the theoretical.

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0.1608 g of the substance weighed in; 0.0709 g As_2S_5

0.1412 g of the substance weighed in; 22.25 ml NaOH

1 ml NaOH; 0.5448 mg P

Found % of As: 21.30; found % of P: 8.59

Computed % of As: 21.16; found % of P: 8.76

d_0^{20} 1.1087; n_D^{20} 1.4738

$C_{14}H_{32}AsPO_3$

This viscous liquid was very rapidly oxidized with liberation of heat upon contact with the air.

Preparation of n-propyl Ester of Ethylphenylcacodylphosphonic Acid

Preparation of this compound was accomplished by the interaction of the sodium salt of dipropylphosphorous acid, which had previously been prepared from 2.17 grams of metallic sodium and 19.3 grams of dipropylphosphoric acid with 35 grams of ethylphenyliodoarsine. Distillation in a stream of CO_2 in a vacuum gave the following fractions:

I. 140-165° at 2 mm - 4.65 g

II. 165-167° at 2 mm - 18.26 g

Residue in the flask - 8.52 g

A subsequent distillation of the second fraction yielded a fraction the boiling point of which is given in the table.

0.1269 g of the substance weighed in; 0.0572 g As_2S_5

0.1152 g of the substance weighed in; 18.1 ml NaOH

1 ml NaOH; 0.5535 mg P

Found % of As: 21.78; P: 8.69

Computed % of As: 21.65; P: 8.96

$C_{14}H_{24}AsPO_3$

d_0^{24} 1.2427; n_D^{24} 1.5375

Preparation of Butyl Ester of Ethylphenylcacodylphosphonic Acid

A yield of 60.7 percent of the theoretical or 15 grams was obtained from 2.2 grams of metallic Na, 20 grams of dibutylphosphorous acid, and 30 grams of ethylphenyliodoarsine.

0.1319 g of the substance weighed in; 0.0552 g As_2S_5

I. 0.1312 g of the substance weighed in; 19.6 ml NaOH

II. 0.1361 g of the substance weighed in; 20.1 ml NaOH 1 ml NaOH; 0.5535 mg P

SECRET

Found % of As: 20.22; found % of P: I-8.27; II-8.17

Computed % of As: 20.03; computed % of P: 8.28

d_0^{13} 1.1875; n_D^{18} 1.5304

A viscous liquid with the molecular formula $C_{16}H_{28}AsPO_3$, this compound oxidizes in the air to form bis-(ethylphenylarsyl)-oxide with a boiling point 188-189 degrees at 5 millimeters.

Saponification of Butyl Ester of Ethylphenylcacodylphosphonic Acid

Seven grams of the substance and 20 milliliters of concentrated hydrochloric acid were heated in a flask with a reflux condenser for 6 hours. After cooling, the contents of the flask separated into two layers, the lower one of which was then removed, washed with water, and dried with calcium chloride. The boiling point (187-188 degrees at 4.5 millimeters and other physical constants indicated that the compound obtained was bis-(ethylphenylarsyl)-oxide, earlier prepared by Kamay (4).

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